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An acid bath for the electrodeposition of glossy gold and gold alloy layers and a gloss additive for same

Description:

The invention provides an acid bath for the  
5 electrodeposition of glossy gold and gold alloy layers and a gloss additive for same.

Electroplating gold baths usually contain gold and optionally one or more alloy elements in dissolved form.

10 These types of electrolytes are mainly based on gold cyanide complexes. It is necessary to adjust these electrolytes to a weakly to moderately acid pH by using inorganic and/or organic acids and buffer salts.

15 So that glossy gold or gold alloy layers are deposited from such baths, these usually contain specific inorganic or organic compounds as so-called "gloss additives".

A typical, very frequently used gloss additive is, as described for example in DE 23 55 581, the compound pyridine-3-sulfonic acid.

20 These types of additive shift or extend the working range which can be used, that is the range of current densities within which a glossy gold coating is deposited, in the direction of higher current densities. There again, the use of higher current densities enables deposition to proceed at a greater rate.

25 On the other hand, the working range of these types of gold baths also depends on the pH of the electrolytes. This means that if the pH is higher the working range (current density range which can be used) becomes narrower, but at the same time the current efficiency, and  
30 thus the rate of deposition, is increased.

Therefore, the object of the invention was to optimise the working conditions and deposition performance in these types of gold baths in such a way that on the one hand a maximum current density/working range is produced with the 5 smallest possible negative effect when the pH is changed and on the other hand a maximum current efficiency and rate of deposition is achieved.

Surprisingly, it has now been found that this can be achieved if at least one compound of the general formula I 10 is added as a further gloss additive to these types of baths for deposition of glossy gold layers,

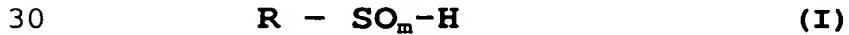


wherein

$m$  is the number 3 or 4, and

15  $\text{R}$  represents a straight-chain or branched or cyclic alkyl group with up to 20 carbon atoms and, in the event that  $m = 4$ , also an aryl or heteroaryl group with up to 10 carbon atoms, which may be optionally substituted once or several times with 20 straight-chain or branched alkyl groups with 1 to 14 carbon atoms.

Thus, the invention provides an acid bath for the electrodeposition of glossy gold and gold alloy layers 25 containing gold and optionally one or more alloy elements in dissolved form and also at least one organic compound as a gloss additive, characterised in that the bath contains, as a further gloss additive, at least one compound of the general formula



wherein

m is the number 3 or 4, and

R represents a straight-chain or branched or cyclic alkyl group with up to 20 carbon atoms and, in the event that m = 4, also an aryl or heteroaryl group with up to 10 carbon atoms, which may be optionally substituted once or several times with straight-chain or branched alkyl groups with 1 to 14 carbon atoms.

10 Gloss additives in accordance with formula I are chosen from the classes consisting of alkyl sulfonates and alkyl, aryl or heteroaryl sulfates. In formula I, if m is the number 3 or 4 then R represents a straight-chain or branched or cyclic alkyl group with up to 20 carbon atoms.

15 If m is the number 4 than R may also represent an aryl or heteroaryl group with up to 10 carbon atoms, wherein these may be substituted once or several times with straight-chain or branched alkyl groups with 1 to 14 carbon atoms.

20 Compounds of the formula I are known per se and are either commercially available or can easily be prepared by standard processes.

These compounds are sufficiently soluble in water and are compatible with the electrodeposition bath. The compounds have surfactant properties, wherein the corresponding 25 effect is reduced when the total number of carbon atoms is less than 4 and generally sufficient solubility is no longer exhibited when the total number of carbon atoms is greater than 20.

Preferred gloss additives are compounds of the formula I 30 in which R represents straight-chain or branched or cyclic alkyl groups with 5 to 12 carbon atoms and in particular for branched alkyl groups with 6 to 10 carbon atoms.

Typical gloss additives according to the invention are

pentyl sulfonate	pentyl sulfate
hexyl sulfonate	hexyl sulfate
heptyl sulfonate	heptyl sulfate
5 octyl sulfonate	octyl sulfate
nonyl sulfonate	nonyl sulfate
decyl sulfonate	decyl sulfate
dodecyl sulfonate	dodecyl sulfate
cyclohexyl sulfonate	cyclohexyl sulfate

10 and their isomers.

These compounds may also be present in the form of their salts.

Branched and short-chain compounds are particularly suitable due to their low tendency to pronounced foam production, in particular in processes and plant in which severe foam production could cause problems, e.g. in the case of air-stirred electrolytes, when processing in drums, in plants for high-speed deposition (spray plants) and in plants for selective deposition such as e.g. dipping cells.

The use of the further gloss additive according to the invention in acid baths for the electrodeposition of glossy gold and gold alloy layers expediently takes place in the concentration range from 0.01 to 10 g/l. Baths according to the invention which contain the gloss additive in accordance with formula I at a concentration of 0.1 to 5 g/l are particularly advantageous.

Due to the use according to the invention of compounds of compounds (sic) of the formula I as a further gloss additive in electrodeposition gold baths with an otherwise conventional composition, the current density/working

range which can be used is considerably extended in an unexpected manner and at the same time the current efficiency and the deposition performance are sometimes drastically increased.

5 To prepare gold baths according to the invention, many commonly used and commercially available weakly acidic gold baths may be used as the starting composition to which a corresponding amount of the compound of the formula I is added. The qualitative and quantitative  
10 composition of these types of gold baths is extremely well-known to a person skilled in the art from literature and from practice and therefore does not require a detailed explanation. In every case, these contain gold in dissolved form, obtained from gold salts or gold complex  
15 salts, wherein mainly gold cyanide complexes are used. Furthermore, the baths may contain alloy elements in the form of dissolved salts or complex salts. Furthermore, the baths contain inorganic and/or organic acids, corresponding salts and optionally buffer and supporting  
20 electrolytes in order to adjust the pH and the conductivity. In order to deposit glossy, smooth gold layers, organic compounds are generally contained therein, these mostly having surfactant properties and acting as a gloss-producer. A typical and well-proven gloss-producer  
25 of this type is pyridine-3-sulfonic acid.

Furthermore, the following compounds and their salts and derivatives are also suitable as conventional gloss additives:

nicotinic acid

30 nicotinamide

3-(3-pyridyl)-acrylic acid

3-(4-imidazolyl)-acrylic acid

3-pyridylhydroxymethanesulfonic acid

pyridine

picoline

quinolinesulfonic acid

5 3-aminopyridine

2,3-diaminopyridine

2,3-di-(2-pyridyl)-pyrazine

2-(pyridyl)-4-ethansulfonic acid

1-(3-sulfopropyl)-pyridinium betaine

10 1-(3-sulfopropyl)-isoquinolinium betaine

Electrodeposition gold baths according to the invention typically contain about

0.1 - 50 g/l of gold as a gold cyanide complex

15 0 - 50 g/l of alloy elements such as iron, cobalt, nickel, indium, silver, copper, cadmium, tin, zinc, bismuth, arsenic, antimony as a salt or complex salt

20 10- 200 g/l of citric acid/citrate as a buffer and/or supporting electrolyte

0.1 - 10 g/l of pyridine-3-sulfonic acid as gloss-producer

0.1 - 5 g/l of a compound of the formula I as a further gloss additive according to the invention,

wherein the pH of the bath is adjusted to 3 to 6,  
5 preferably 4 to 5.

Use of the gloss additive according to the invention produces a number of practical advantages. Thus, under otherwise unchanged conditions, the deposition performance can be clearly increased. Due to the wider working range,  
10 fine adjustment of the mode of operation is less critical, wherein the risk of defective deposition is greatly reduced.

However, a higher pH may also be used with an unchanged working range. The deposition performance can also be  
15 increased in this way.

Alternatively, however, a smaller gold concentration may be used while retaining the same deposition performance. The advantages associated with this move are the smaller losses due to electrolytes being carried over by adhering  
20 to the goods and the smaller amount of capital which is tied up.

Example 1:

A working range of up to 3 A/dm<sup>2</sup> is produced with a cell  
25 current of 2 A in a coating cell which contains a gold/cobalt electrolyte containing

10 g/l of gold in the form of potassium gold(I)  
cyanide  
0.5 g of cobalt as cobalt sulfate  
30 100 g/l of citric acid  
3 g/l of pyridine-3-sulfonic acid.

adjusted to pH 4.2 with potassium hydroxide,  
5 (trial conditions: platinised titanium anode, temperature  
50°C, time 2 min, agitated at 500 rpm with a 25 mm  
magnetic stirring rod). The current efficiency at 3 A/dm<sup>2</sup>  
is 48 %; the rate of deposition is 0.98 µm/min.

By adding 1 g/l of nonyl sulfate, the maximum current  
density which can be used is increased to more than  
5 A/dm<sup>2</sup>. This corresponds to extending the working range by  
10 more than 66 %.

If the pH is then raised to 4.4, a working range of up to  
4 A/dm<sup>2</sup> is produced; the deposition performance is  
1.05 µm/min.

At a pH of 4.6 the working range extends up to 3 A/dm<sup>2</sup> and  
15 a rate of deposition of 1.15 µm/min is produced.

Example 2:

A maximum current density of 3 A/dm<sup>2</sup> is achieved in a  
gold/nickel electrolyte containing

20 10 g/l of gold in the form of potassium gold(I)  
cyanide  
0.7 g of nickel in the form of nickel sulfate  
100 g/l of citric acid  
3 g/l of pyridine-3-sulfonic acid,  
25 adjusted to pH 4.2 with potassium hydroxide,

on pre-nickel-coated sheets with the dimensions 25 x 40 mm  
(trial conditions: 1 litre glass beaker, platinised  
titium anode, bath agitated at 200 rpm using a 60 mm  
magnetic stirring rod, goods moved at 5 cm/s). The  
30 cathodic current efficiency at 3 A/dm<sup>2</sup> is 52 % and the rate  
of deposition is 1.0 µm/min.

By adding 0.5 g/l of decyl sulfate, the maximum current density which can be used is increased to more than 7 A/dm<sup>2</sup>. At 7 A/dm<sup>2</sup> the current efficiency is still 26 %, the deposition performance increases to 1.18 µm/min. This corresponds to increasing the rate by 18 %.

Example 3:

A maximum current density of 5 A/dm<sup>2</sup> is achieved in a gold/iron electrolyte containing

- 10      10 g/l of gold in the form of potassium gold(I)  
cyanide  
10      0.05 g of iron as iron (III) citrate  
100 g/l of citric acid  
10      3 g/l of pyridine-3-sulfonic acid,  
adjusted to pH 4.2 with potassium hydroxide,  
15      on sheets with the dimensions 25 x 40 mm (for conditions,  
see example 2). The cathodic current efficiency is 31 %  
and the rate of deposition is 1.0 µm/min.

By adding 4 g/l of hexyl sulfate the maximum current density which can be used is increased to more than 20 6 A/dm<sup>2</sup>. At 6 A/dm<sup>2</sup> the current efficiency is still 30 %; the deposition performance increases to 1.16 µm/min. This corresponds to increasing the rate by 16 %.

Example 4:

- 25      A working range of up to 5 A/dm<sup>2</sup> is produced in a coating cell with a cell current of 2 A in a gold/cobalt electrolyte containing

30      10 g/l of gold in the form of potassium gold(I)  
cyanide  
30      0.5 g of cobalt as cobalt sulfate  
100 g/l of citric acid

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1 g/l 3-(3-pyridyl)-acrylic acid,  
adjusted to pH 4.2 with potassium hydroxide,

(trial conditions: platinised titanium anode, temperature 50°C, time 2 min, agitated at 500 rpm with a 25 mm magnetic stirring rod). The current efficiency at 5 A/dm<sup>2</sup> is 26 %; the rate of deposition is 0.83 µm/min.

By adding 1.5 g/l of octyl sulfate the maximum current density which can be used is increased to more than 8 A/dm<sup>2</sup>. At 8 A/dm<sup>2</sup> the current efficiency is still 19 %;

10 the deposition performance increases to 1.0 µm/min.

Example 5:

In the gold/cobalt electrolyte from example 1, the maximum current density which can be used is increased to more  
15 than 5 A/dm<sup>2</sup> by adding 1 g/l of hexyl sulfonate. At 5 A/dm<sup>2</sup> the current efficiency is 35.1 %, the deposition performance is increased to 1.13 µm/min. This corresponds to increasing the rate by 15 %.

20 Example 6:

In the gold/cobalt electrolyte from example 1, the maximum current density which can be used is increased to more than 7 A/dm<sup>2</sup> by adding 1 g/l of octyl sulfonate. At 7 A/dm<sup>2</sup> the current efficiency is 26.2 %, the deposition  
25 performance increases to 1.18 µm/min. This corresponds to increasing the rate by 20 %.

Example 7: Comparison example

In a gold/cobalt electrolyte (see example 1) consisting of

10 g/l of gold in the form of potassium gold(I) cyanide

0.5 g of cobalt as cobalt sulfate

100 g/l of citric acid,

5 adjusted to pH 4.2 with potassium hydroxide,

and using the trial conditions in example 1, the effect on the working range and the rate of deposition was determined when adding only octyl sulfate, only pyridine-3-sulfonic acid and both substances together as a gloss additive. The results are given in table 1.

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The combination of the two substances greatly extends the working range and causes a considerable increase in the rate of deposition.

Table 1:

Octyl sulfate	Pyridine-3-sulfonic acid	Working range (gloss) up to	Rate of deposition
-	-	2 A/dm <sup>2</sup>	0.63 µm/min
2 g/l	-	2 A/dm <sup>2</sup>	0.65 µm/min
-	3 g/l	3 A/dm <sup>2</sup>	0.98 µm/min
2 g/l	3 g/l	5 A/dm <sup>2</sup>	1.12 µm/min

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